



Short communication

Triplite LiFeSO_4F as cathode material for Li-ion batteriesJinping Dong^a, Xiqian Yu^b, Yang Sun^a, Lei Liu^a, Xiaoqing Yang^b, Xuejie Huang^{a,*}^a Institute of Physics, Chinese Academy of Science, Beijing 100190, China^b Brookhaven National Laboratory, Upton, NY 11973, USA

H I G H L I G H T S

- ▶ The triplite-phase LiFeSO_4F was obtained by solid state reactions.
- ▶ Not 100% Li can be extracted from the lattice by XANES.
- ▶ A core–shell model was mentioned to explain the polarization phenomenon.

A R T I C L E I N F O

Article history:

Received 1 October 2012

Received in revised form

22 November 2012

Accepted 23 November 2012

Available online 1 December 2012

Keywords:

Fluorosulphate

Cathode material

Lithium ion batteries

Cation mixing

A B S T R A C T

Monoclinic phase LiFeSO_4F has a triplite like structure in which $\text{Li}^+/\text{Fe}^{2+}$ is fully mixing. Not 100% Li can be extracted from the lattice easily even at a rate of C/20, and the valence of Fe changes between $\text{ca } +2$ and $+2.5$ observed by XANES for a $\text{Li}/\text{LiFeSO}_4\text{F}$ cell cycled between 2.2 and 4.6 V. Two-phase reaction mechanism is verified by GITT due to the appearance of a flat plateau, and large polarization appears after more than 50% Li extracted from triplite- LiFeSO_4F . A core–shell model has been mentioned to explain its extreme polarization. In the fully mixing structure, there is no intact long-range pathway for Li^+ , so leading to sluggish kinetics effect and “inert” Li^+ in the lattice.

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1. Introduction

Rechargeable lithium-ion batteries (LIBs) are the core technology in the era of advanced portable electronics and electric transportation [1]. Most of current research is directed to advanced electrode materials with high capacity, high safety and low cost, especially on cathode materials which determine energy and power densities of LIBs [2], such as olivines (LiFePO_4) proposed by Pahdi et al. [3,4], poly-anion compound LiFePO_4 has been thoroughly investigated and recognized as the most promising cathode material for LIBs. Meanwhile, other low-cost and abundant poly-anion materials were also been investigated, e.g. silicates (LiM-SiO_4 [5,6]), borates (LiMBO_3 [7]), and fluorophosphates ($\text{A}_2\text{MPO}_4\text{F}$ [8]). As we know, the redox potential is 3.45 V vs. Li/Li^+ for LiFePO_4 due to the inductive effect of PO_4^{3-} . In an attempt to increase the energy density of these polyanion materials, replacing PO_4 tetrahedra by F and SO_4 tetrahedra which have larger electronegativity is a feasible way for getting this goal. In 2009, Recham et al. [9] reported the reversible Li insertion/extraction in tavorite- LiFeSO_4F

(triclinic phase) with redox potential 3.6 V. In 2011, Liu and Barpanda et al. [10,11] reported the triplite- LiFeSO_4F (monoclinic phase) with redox potential 3.9 V in which $\text{Li}^+/\text{Fe}^{2+}$ is fully mixing. The unique cation-mixing structure does not block the Li^+ diffusion because it has a quasi three dimensional network for Li ion migration with activation energy ranges from 0.53 to 0.69 eV [12], comparable with LiFePO_4 which only has one dimensional channel for Li ion. However, we found that not 100% Li can be extracted from the lattice even at a very low rate by XANES. And also, polarization increased dramatically after more than 50% Li extracted from triplite- LiFeSO_4F observed from a GITT test. Meanwhile, a core–shell model [13] has been proposed to explain this phenomenon. Of course, the extreme polarization is also reasonably attributed to its cation-mixing structure, in which there is no intact long-range pathway for Li^+ .

2. Experiments

2.1. Synthesis

Stoichiometric amounts of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (Alfa Aesar, 99%), LiF (Sinopharm Chemical Reagent Co. Ltd, 99%) and multi-wall carbon

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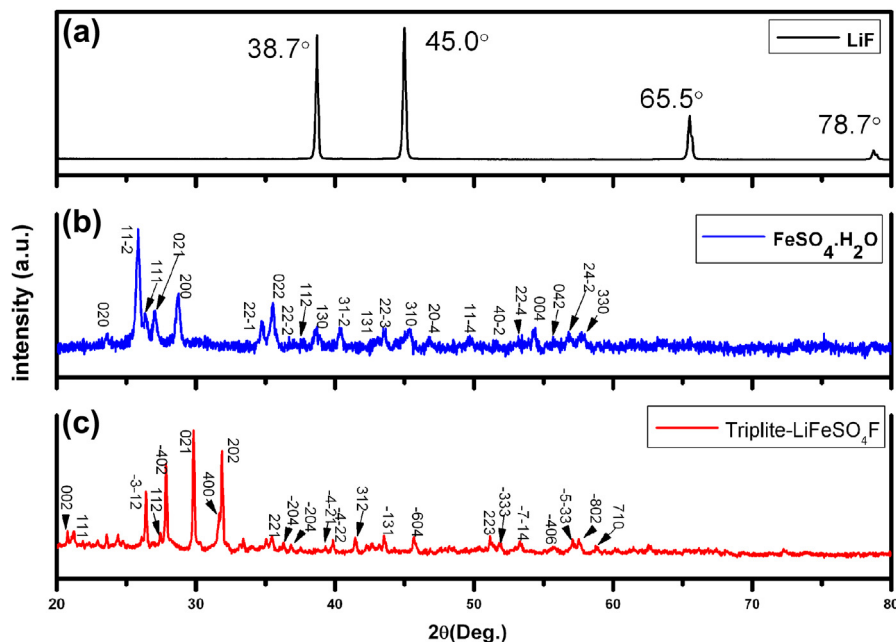


Fig. 1. The XRD of LiF (a), the mixture after HEBM (b) and triplite-LiFeSO₄F (c).

nano-tubes (MW-CNTs, 3wt.%, CNano Technology Ltd) were mixed using high energy ball milling (HEBM, Union Process 01-HD) with alcohol in a zirconia container for 8 h before heating treatment.

The triplite-phase LiFeSO₄F was obtained by a following heating treatment at 370°C (at a heating rate of $10^\circ\text{C min}^{-1}$) and 4 MPa under ambient pressure of *ca* 10 Pa for 60 h.

2.2. Characterizations

The X-ray diffraction patterns were collected using a X'Pert Pro MPD X-ray diffractometer (Philips, Holland) with Cu K α radiation ($\lambda = 1.5405 \text{ \AA}$, operating at 40 kV and 30 mA) at a scan rate of $0.02^\circ (2\theta) \text{ s}^{-1}$. The morphology of all samples was observed by a field-emission gun scanning electron microscope (Hitachi S-4800), operating at 10 kV under low vacuum to avoid any charging effect.

Fe K-edge XANES spectra were collected in transmission mode at beam line X18A (NSLS, USA.) using a Si (111) double-crystal monochromator detuned to the 35–45% value of its original maximum intensity to eliminate the high order harmonics. Reference spectrum of each element was simultaneously collected with the corresponding spectrum of the *in-situ* cells using Fe metal foil. Energy calibration was carried out using the first inflection point of the K-edge spectrum of Fe metal foil as reference (i.e., Fe: 7112 eV).

Electrochemical characterization was conducted using Swagelok-type cells. Cathodes consisted of active powder

material (80 wt.%), acetylene black (10 wt.%) and polyvinylidene fluoride (PVDF, 10 wt.%), and Al foil was used as the current collector. All cells were assembled inside an argon-filled glovebox and all electrochemical tests were performed using a half cell with a Li counter electrode, 1 M LiPF₆ EC/DMC (1:1 by volume) electrolyte, and Celgard™ 2400 separator. The galvanostatic charge–discharge tests were performed using a Land™ automatic batteries tester (KINGNUO Electrical Co. Ltd., China) at 25°C . The cells were typically cycled between 2.5 V and 4.5 V vs. Li/Li⁺ at a rate of C/20 and C/30. At the third cycle, the galvanostatic intermittent titration technology (GITT) test was performed between 2.5 V and 4.5 V by charging/discharging the cell for 30 min at a constant rate of C/20 and by relaxing for 12 h.

3. Results and discussion

3.1. Structure and morphology

In the mixture after milling, FeSO₄·H₂O phase exists and almost no LiF (diffraction angle $2\theta = 38.7^\circ, 45.0^\circ, 65.5^\circ$, Fig. 1a) and MW-CNTs can be observed by XRD (Fig. 1b) due to small particle size obtained from HEBM. And from the SEM images (Fig. 2), it can be seen that the particle size of precursor is $\sim 45 \text{ nm}$ after HEBM and MW-CNTs disperse evenly in the mixture.

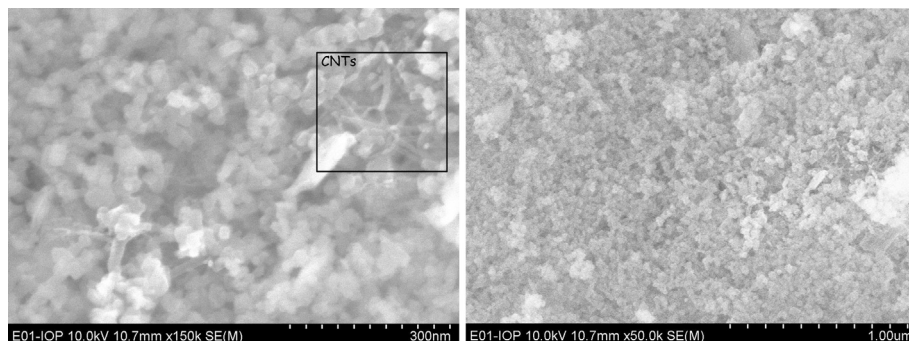


Fig. 2. The SEM images of the precursors with CNTs.

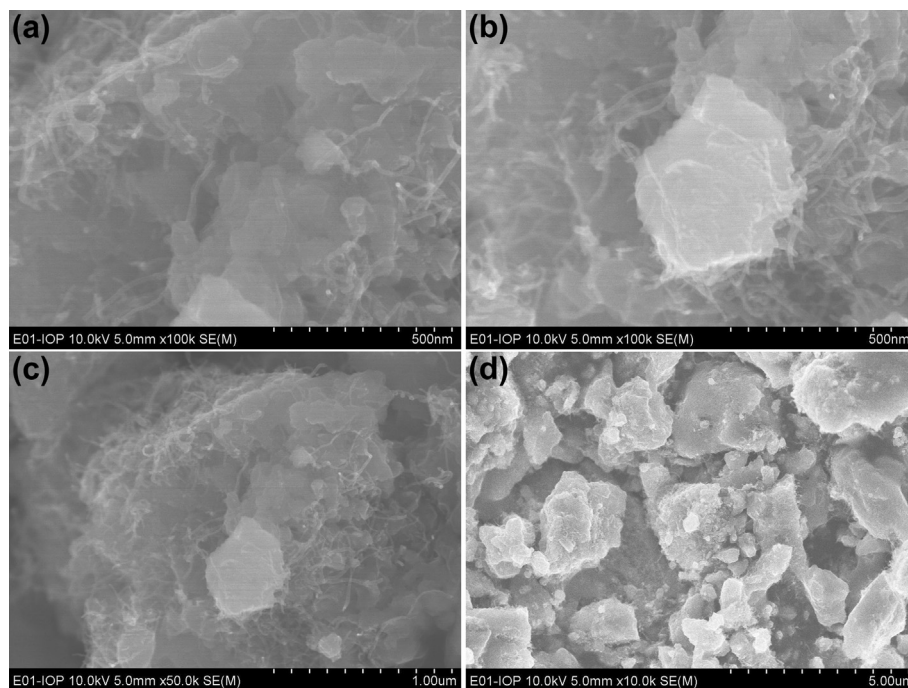


Fig. 3. The SEM images of as prepared triplite-LiFeSO₄F.

The as prepared triplite-phase LiFeSO₄F obtained by heating treatment was confirmed by XRD and the diffraction index have been labeled (Fig. 1c).

From the SEM images (Fig. 3), it can be seen that the particle size ranges from few nanometers to few micrometers. However, the large particles are agglomerates of nano size LiFeSO₄F and CNTs. Large size particle has long distance for lithium diffusion and limits

its kinetic properties. But the dispersed CNTs in the specimen may be helpful for the electronic conductance.

3.2. Electrochemical properties

Fig. 4 shows the charge and discharge curves for the triplite-LiFeSO₄F at 25 °C in the range of 2.5–4.5 V from 1st cycle to 60th

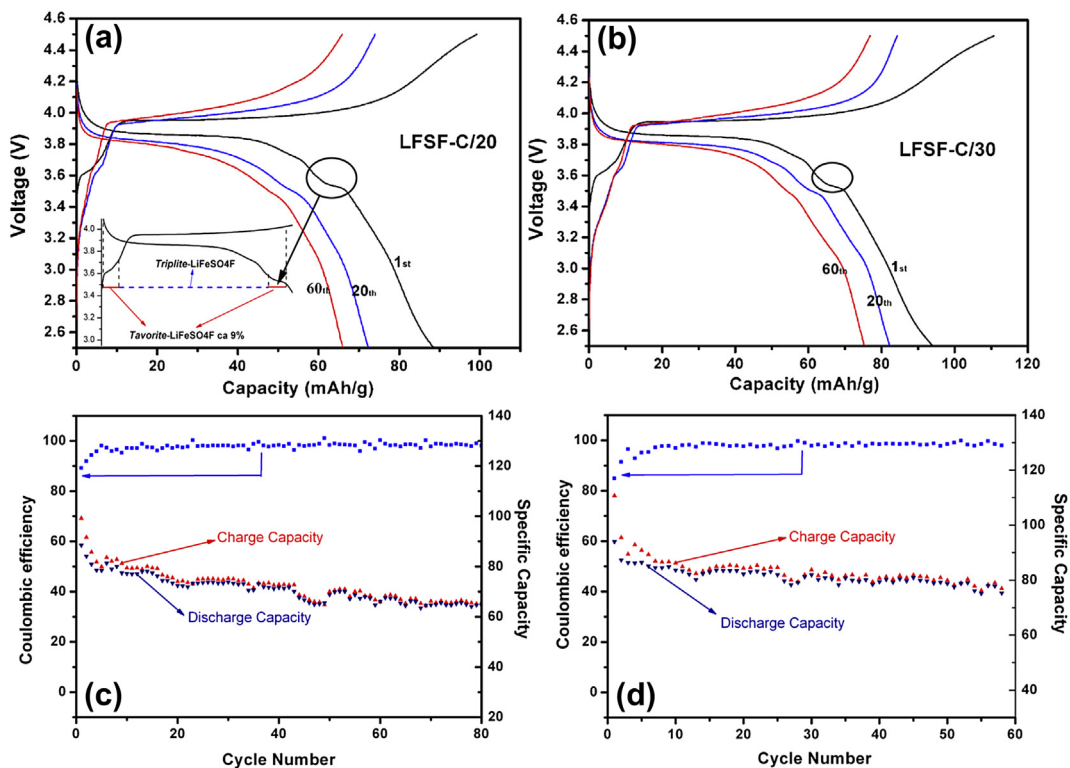


Fig. 4. Galvanostatic charge and discharge curves for triplite-LiFeSO₄F. The capacity retention during a C/20 rate (c) and a C/30 rate (d).

cycle. In Fig. 4(a) and (b), a flat plateau was observed around 3.9 V which was also confirmed by GITT (see Fig. 5). It is attributed to the two-phase reaction of the $(1-x)\text{FeSO}_4\text{F} + x\text{LiFeSO}_4\text{F}$ system. However, about 10% of the capacity is attributed to the tavorite- LiFeSO_4F with 3.6 V vs. Li/Li^+ (Fig. 4a, inset) in the 1st cycle. But, the 3.6 V plateau was changed to a slope in the later cycles. It seems that the corresponding tavorite phase became amorphous in the following cycles. As shown in Fig. 4(c), the measured first cycle discharge capacity is 88.5 mAh g^{-1} at a rate of C/20. In Fig. 4(d), while it is 94 mAh g^{-1} at a rate of C/30. And the initial Coulombic efficiencies are only 84.9% and 89.2% respectively, indicating a sluggish kinetics for this cation mixed material.

In the third cycle, the GITT test was performed. A 3.9 V plateau clearly indicates a two-phase reaction mechanism. Meanwhile, not 100% Li can be extracted in the GITT measurement due to the cation-mixing structure, and larger polarization appeared when more than 50% Li extracted from triplite- LiFeSO_4F . Generally, the polarization is related to the stress-strain in the charge–discharge process or there is not enough long relaxed time in the GITT test. As we know, the volume change of triplite- LiFeSO_4F is very small (*ca* 1%) [11,12], so the effect of stress-strain on the polarization can be neglected. Hence, the large polarization might be attributed to the sluggish ionic diffusion kinetics, and the cell cannot reach an equilibrium state in 12 h. A core–shell model [13] can be used to describe the mechanism. At the beginning, tavorite phase is dispersed in the sample and Li^+ can be extracted at lower potential. But a larger polarization is reasonable because most of the extracted Li^+ must pass through the triplite phase. Once the Li^+ was completely extracted from the tavorite phase, Li^+ from the outer layer of triplite phase starts to come out, and a lower polarization appears (Region A). Larger polarization appeared again when the diffusion length of Li^+ through the core increased irregularly. After *ca* 50% Li^+ ($\sim 76\text{ mAh g}^{-1}$) in the triplite phase was get out, the polarization increased dramatically (200–500 mV) due to that delithium- FeSO_4F covered LiFeSO_4F completely. However, a small amount of tavorite-phase (3.6 vs. Li/Li^+) which has better kinetic effect [9], in the Region B. The extreme large polarization compared with other Fe-based polyanion materials, e.g. olivine- LiFePO_4 and tavorite- LiFeSO_4F , should be reasonably attributed to its cation-mixing nature. As can be seen from the insets of Fig. 5, Fe ions randomly occupy two independent Li/Fe sites. Although DFT calculations show a quasi-three dimensional (3D) network for Li diffusion [12], Fe ions in front of the Li-diffusion path should always be expected, leading to no intact long-range channel for Li transportation in such

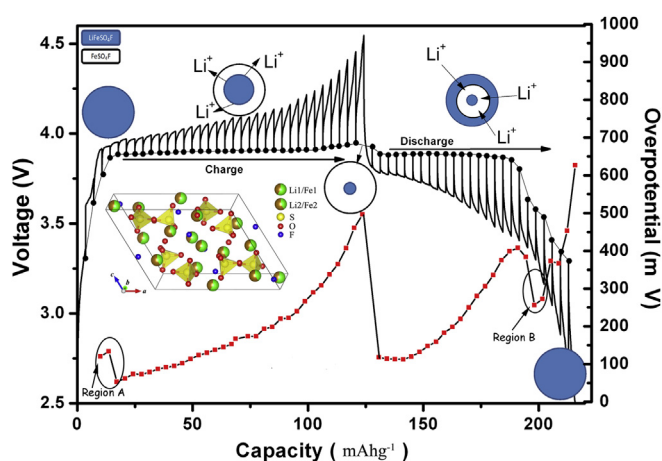


Fig. 5. GITT and ohmic polarization curves of triplite- LiFeSO_4F during charging and discharging at the third cycle. Colour insets: Crystal structure and diffusion model.

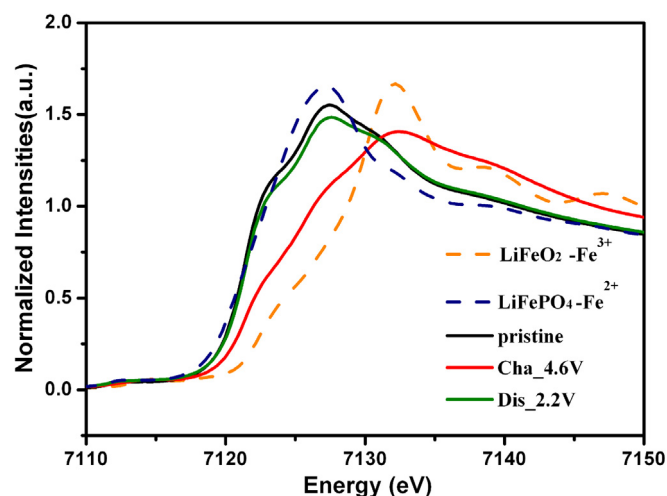


Fig. 6. The Fe K-edge XANES spectra of triplite- LiFeSO_4F in charge to 4.6 V and discharge to 2.2 V using a C/20 rate.

a lattice structure. The resulting intrinsically low ionic conductivity is in consistent with our experimental measurements: even by providing the excellent electronic conducting network (CNTs) and keeping the small grains, the polarization is still much higher than other existing electrode materials for LIBs. Besides the low Li diffusion kinetics, the random Li/Fe distribution may cause some “inert” Li^+ , as the pathways of Li ions encompassed by Fe ions are completely blocked and therefore cannot be extracted (see insets of Fig. 5) totally. Consequently, it is difficult, or even impossible, for us to achieving the theoretical capacity.

In Fig. 6, the valence change of Fe was analyzed by XANES and compared with that of LiFeO_2 and LiFePO_4 respectively. It changes between *ca* +2 and +2.5 for a $\text{Li}/\text{LiFeSO}_4\text{F}$ cell cycled between 2.2 and 4.6 V using a rate of C/20. Therefore, not 100% Li can be extracted even at such a rate, due to its sluggish kinetics.

4. Conclusion

Monoclinic phase LiFeSO_4F is a cathode material for Li-ion battery with 3.9 V vs. Li/Li^+ . It has a triplite-like structure in which $\text{Li}^+/\text{Fe}^{2+}$ is fully mixing, but Li^+ diffusion is not blocked because it has a three dimensional network for Li ion migration. While its theoretical capacity is 151 mAh g^{-1} , the measured first cycle discharge capacity is 88.5 mAh g^{-1} using a rate of C/20 or 94 mAh g^{-1} using a rate of C/30 and the initial Coulombic efficiencies are 84.9% and 89.2% respectively. From Fe K-edge XANES spectra, it is observed that valence of Fe changes between *ca* +2 and +2.5 for a $\text{Li}/\text{LiFeSO}_4\text{F}$ cycled between 2.2 and 4.6 V using a C/20 rate, due to its sluggish kinetics. Two-phase reaction mechanism is verified by GITT, and large polarization appears when more than 50% Li extracted from triplite- LiFeSO_4F . A core–shell model can be used to explain its extreme polarization. There is not intact long-range pathway for Li^+ and only a limited capacity can be obtained at reasonable rates.

Acknowledgment

This work was supported by Hi-tech Research and Development Program of China (2009AA033101). The work at Brookhaven National Lab. was supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Vehicle Technologies of the U.S. DOE under Contract No. DE-AC02-98CH10886. Research at beam line X14A and X18A were partially sponsored by the U.S. DOE. The authors thank the help from Dr. Steven N. Ehrlich.

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